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(54) Title: POURABLE ORGANIC ACID-BASED GRANULATES, PROCESS FOR THEIR PREPARATION AND THEIR USE

(54) Bezeichnung: RIESELFÄHIGES GRANULAT AUF BASIS ORGANISCHER SÄUREN, VERFAHREN ZU SEINER HERSTELLUNG UND SEINE VERWENDUNG

(57) Abstract

The invention concerns pourable granulates comprising a core and a casing, characterized in that the core material contains an organic acid and a porous carrier, and the casing comprises a covering agent which is water-soluble or can swell in water at 20 °C.

(57) Zusammenfassung

Rieselfähiges Granulat, bestehend aus einem Kern und einer Hülle, dadurch gekennzeichnet, daß das Kernmaterial eine organische Säure und einen porösen Träger enthält und die Hülle ein bei 20 °C wasserlösliches oder wasserquellbares Abdeckmittel aufweist.

Free-flowing granules based on organic acids, preparation of said granules and their use

Abstract

In free-flowing granules consisting of a core and a coat, the core material contains an organic acid and a porous carrier and the coat has a covering material which is water-soluble or water-swellable at 20°C.

Free-flowing granules based on organic acids, preparation of said granules and their use

The present invention relates to free-flowing granules consisting of a core and of a coat, wherein the core material contains an organic acid and a porous carrier and the coat has a water-soluble or water-swellable covering material.

The present invention furthermore relates to a process for the preparation of free-flowing, low-odor granules based on organic acids, preferably formic, acetic and/or propionic acid, and to the use of the granules for the treatment of foods and animal feeds, and to their use in silages.

Short-chain organic acids, such as formic acid, acetic acid or propionic acid, are used in the acidification and preservation of foods and animal feeds. The disadvantages of these acids are (a) their liquid state of aggregation at room temperature, (b) the sharp, pungent odor resulting from the low vapor pressure and (c) their corrosiveness.

Furthermore, the liquid organic acids in concentrated form can be incorporated, for example in animal feeds, only by the considerably complicated technical procedure.

DE 28 33 727 A1 discloses a particulate, fungicidal material which contains propionic acid and a carrier. This material is intended to prevent an increase in the number of mold colonies in stored agricultural harvest products even with an incubation time of several days. However, it has been found that such material is itself not stable when stored (loss of acid), and the maximum amount of propionic acid which can be applied depends to a great extent on the carrier used. In addition, unpleasant odors occur with this material owing to the volatility of the propionic acid.

It is an object of the present invention to provide free-flowing, low-odor granules for the treatment of foods and animal feeds, by means of which the handling properties are substantially improved for the user. Attention was focussed on the preparation of a solid organic acid in the form of an adsorbate which was to differ from simple impregnated products essentially in that it (a) permits an acid content > 30% by weight in the solid regardless of the carrier and hence has a very high active ingredient content and (b) the release of the organic acid from the adsorbate is kept to a minimum and hence the active ingredient content is

maintained. The pulverulent end product should have good storage, flow and processing properties.

We have found that this object is achieved by granules consisting of a core and a coat, wherein the core material contains an organic acid and a porous carrier and the coat has a covering material which is water-soluble or water-swellable at 20°C.

The novel granules have the advantage that the highly pungent acid odor is reduced and, in spite of the solid formulation, the acid content is released from the solid powder in readily and rapidly soluble form.

The present invention furthermore relates to a process for the preparation of granules containing organic acids and porous carriers, which comprises impregnating the carrier with the liquid organic acid, then agglomerating it with a covering material which solidifies at room temperature, the covering material being added in an amount such that the resulting granules are coated, and, if required, providing a further odor by adding scents and, if required, ensuring free-flowing properties of the agglomerates by dusting with a finely divided dusting agent.

The liquid organic acid is understood as meaning acids or acid mixtures which are liquid at the processing temperatures or are converted into the liquid state by increasing the temperature or dissolving or dispersing in liquids.

In a preferred embodiment, the novel granules have a dusting agent on the surface of the coat. The core contains preferably 30-90, in particular 50-80, % by weight of organic acid. The organic acid preferably consists of one or more C_1-C_6-mono- or dicarboxylic acids, in particular formic, acetic and/or propionic acid.

Suitable carriers are porous, organic or inorganic carriers whose particle sizes are from 1 to 1000 µm, preferably from 5 to 100 µm. The core may also contain further solids, for example solids suitable as feed supplements, such as calcium propionate.

Water-soluble polymers, organic acids, salts thereof or inorganic salts having a low melting point may be used as the covering material.

Cereal brans, silicates, perlite or silicas, in amounts of from 10 to 70, preferably from 20 to 40, % by weight, based on the weight of the core, are preferably used as the carrier.

Preferably used covering materials are polyethylene glycols, polyvinylpyrrolidones or C_3-C_{14}, preferably C_3-C_6, organic acids and salts thereof, in particular citric acid, fumaric acid, succinic acid, adipic acid, benzoic acid and salts thereof, or amino acids and salts thereof are preferably used as the covering material.

In a preferred embodiment of the novel process, the carrier is initially taken in a mixer, impregnated with the organic acid and then agglomerated and coated with the covering material.

The loose and impregnated carrier particles are mixed with the covering material (binding liquid), the binding liquid generally consisting of a highly concentrated solution or melt of water-soluble or water-swellable substances which solidify at room temperature (20°C). This binding liquid is preferably applied in the heated state to the impregnated carrier particles and mixed with the latter. The binding liquids solidify on the surface of the impregnated carrier particles. Suitable operating parameters of the mixer result in agglomeration of different particles to give larger granules.

The size of the granules can be established by process parameters in the mixing as well as by subsequent sieving or milling. The granules preferably have a mean diameter of less than 3 mm, in particular 0.3-1.3 mm. If required, residual water may be present in the binding liquid used for coating and agglomeration. After the agglomeration process, this water can be bound by a dry and finely divided dusting agent by means of a dusting process. As a result of this dusting process, it is also possible to prevent subsequent adhesion of the agglomerates and in addition, for example, to apply the salt of the organic acid used (eg. sodium propionate or calcium propionate) to the agglomerate. Furthermore, a scent or flavor material, eg. vanillin, citral or fructin, can, if required, be added during the dusting step, resulting in an additional odor-masking effect and, for example, ensuring that consumption of the animal feed is appealing.

In principle, all nonorganic or inorganic porous carriers are suitable for the preparation of such free-flowing, low-odor agglomerates, provided that they are acid-resistant. Examples are cereal brands, perlite, clay materials, silicates and silicas,

the inorganic carriers being preferred since their material properties can be more readily controlled.

Preferably used binding liquids are water-soluble or water-swellable substances which solidify at room temperature. This makes it possible to dispense with the subsequent drying step, in which, apart from the solvent and the additional water, the organic acid too would evaporate off in some cases.

Particularly suitable covering materials (binding liquids) for the agglomeration process and the coating are those which have a softening temperature of more than 30°C, preferably more than 60°C, in order to prevent deformation of the agglomerates at a relatively high storage temperature. Covering materials which are preferably to be used are those which furthermore do not counteract the pH-reducing effect of the adsorbed organic acid or, if required, even support or strengthen said effect.

Examples of suitable binding liquids are highly concentrated, heated sugar solutions or alkali metal/alkaline earth metal formate/acetate/propionate solutions. As a result of the final dusting step, the residual water content can be taken up. Polyethylene glycols having a low melting point, eg. PEG 4000, melts of citric acid, of adipic acid, or fumaric acid or of benzoic acid or of salts thereof, highly concentrated solutions of amino acids and mixtures of these acids are preferred as binding liquids. From 5 to 80, preferably from 10 to 25, % by weight, based on the weight of the granules, of binding liquid are used.

Suitable dusting agents in addition to the porous carriers themselves are finely divided, milled organic acids or salts thereof, eg. sodium formate, and inorganic salts or Aerosil. < 10, preferably from 0.5 to 5, % by weight of the dusting agents are added.

In general, the porous carrier is initially taken in the mixer, for example an Eirich mixer, and is impregnated with the organic acid with little energy input. In an alternative procedure, however, the liquid is initially taken in the mixer and the carrier is metered in. In this case, a higher energy input is required.

It is necessary to ensure uniform impregnation and to avoid local overmoistening, which leads to formation of lumps. After impregnation is complete, a free-flowing, slightly cohesive heap of particles is present. The viscosity of the binding liquid should be established by an appropriate choice of temperature so that it is less than 1000, preferably less than 100 mPa.s, in order to achieve a fine drop size distribution when spraying the

binding liquid. Owing to the temperature difference between the heated binding liquid and the cooler impregnated carrier, the drops of binding liquid initially solidify rapidly in this preferred embodiment. In the further course of the agglomeration process, the temperature of the bed increases by 10-30°C, depending on the type of binding liquid, due to the mechanical and the thermal energy input. Further drops of binding liquid accumulate on the agglomerates already formed and some of these drops coalesce with one another. The energy input increases by about 20% during the agglomeration.

Finally, a finely divided odor-imparting material may also be added with the dusting agent, as described above. In principle, a large number of scents and flavor materials are suitable for this purpose and can be chosen in accordance with the subsequent use of the agglomerates. The amount of these scents may be < 1, preferably from 0.05 to 0.5, % by weight, based on the granules. The agglomerates thus produced have a low dust content and little odor and their organic acid content is readily water-soluble.

The novel granules are suitable for the treatment of foods and animal feeds and for use in silages. Foods and animal feeds are to be understood in particular as meaning harvest products, such as hay, silage, moist cereals, pulses or grains, as well as milk substitutes, liquid, mixed and mineral feeds, fish silages or fish meal.

Novel granules may contain other additives, for example minerals, vitamins, antibiotics or protein supplements.

Examples

(Content of formic acid used = 99%/propionic acid used = 99%)

A. Comparative examples

Comparative example 1

100 g of wheat bran are initially taken in a household mixer and impregnated with 100 g of formic acid. The acid is readily taken up; the product exhibits cohesive behavior but can be easily divided up. It has a strong odor of formic acid.

Comparative example 2

100 g of Sipernat® (finely divided silica, from Degussa) are initially taken in a household mixer and impregnated with 100 g of an acid mixture consisting of equal amounts of formic acid and propionic acid. The acid mixture is readily taken up; a loose, free-flowing product forms. The product has a pungent unpleasant odor of formic acid/propionic acid.

Comparative example 3

100 g of perlite are initially taken and are impregnated with the formic acid, similarly to Example 1. The acid is readily taken up but the product shows a strong tendency to cake and has a strong pungent odor of formic acid.

B. Impregnation, agglomeration and coating tests

Example 1

460 g of Sipernat® (finely divided silica, from Degussa) are initially taken in an Eirich mixer (R02) and are impregnated with 905 g of formic acid; the formic acid content is then 67%. 200 g of sodium formate melt at 80°C are then sprayed, as the binding liquid, from a heated storage container via a binary nozzle into the mixing space containing 1000 g of this mixture. The resulting agglomerates are dusted with 44 g of Sipernat®. The content of free acid is 54%. The resulting product is free-flowing and has little odor.

Example 2

400 g of Sipernat® are initially taken in an Eirich mixer and are impregnated with 1000 g of formic acid (formic acid content: 71%). For agglomeration and coating, 180 g of a concentrated dextral solution at 80°C are sprayed, as binding liquid, from a heated storage container via a binary nozzle into the mixing space. The resulting agglomerates are dusted with 45 g of Sipernat® and 12 g of citral. The acid content is then 61%. The resulting agglomerates are free-flowing. The power consumption after the impregnation is ≈ 400 W, and that after coating is ≈ 500 W. The speed is increased from 340 rpm to 460 rpm during the agglomeration step.

Example 3

400g of Sipernat® are initially taken in an Eirich mixer and are impregnated with 1100g of formic acid, similarly to Example 2; the formic acid content is then 71%. 260g of citric acid melt at 170°C are sprayed, as binding liquid, from a heated storage container via a binary nozzle into the mixing space. The resulting agglomerates are dusted with 44g of Sipernat® and 8g of vanillin. The total acid content is ~ 74%. The resulting agglomerates have a substantially reduced odour of formic acid.

Example 4

8.7kg of Sipernat® are initially taken in a ploughshare mixer (Lö 130) and are impregnated with 24kg of formic acid (98%) (formic acid content: 71%). For agglomeration and coating, 5.5kg of citric acid melt at 170°C are sprayed from a heated storage container via a binary nozzle into the mixing space. The resulting agglomerates are dusted with 650g of Sipernat® and 24g of vanillin. The total acid content is ~ 74%. The resulting agglomerates have a substantially reduced odour and are free-flowing.

"Comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Free-flowing granules including of a core and of a coat, wherein the core material contains an organic acid and a porous carrier and the coat has a covering material which is water-soluble or water-swellable at 20°C.

2. Granules as claimed in claim 1, wherein the coat additionally has a dusting agent on the surface.

3. Granules as claimed in claim 1, wherein the core contains 30-90% by weight of organic acids.

4. Granules as claimed in claim 1, wherein the organic acid is a C_1-C_6-mono- or dicarboxylic acid or a mixture of such carboxylic acids.

5. Granules as claimed in claim 1, wherein the carrier used is a porous, organic or inorganic carrier whose particle sizes are from 1 to 1000 µm, preferably from 5 to 100 µm.

6. Granules as claimed in claim 1, wherein the covering material used is a water-soluble polymer, an organic acid, a salt thereof or an inorganic salt having a low melting point.

7. Granules as claimed in claim 5, wherein the carrier used is a cereal bran, a silicate, perlite or a silica, in an amount of from 10 to 70, preferably from 20 to 40, % by weight.

8. Granules as claimed in claim 6, wherein the covering material used is polyethylene glycol, a polyvinylpyrrolidone or a C_3-C_{14}, preferably C_3-C_6, organic acid or a salt thereof, in particular citric acid, fumaric acid, succinic acid, adipic acid, benzoic acid, sorbic acid or a salt thereof or an amino acid or a salt thereof.

9. A process for the preparation of granules containing organic acids and porous carriers, which includes impregnating the carrier with a liquid organic acid, then agglomerating it with a liquefied covering material which solidifies at room temperature, the covering material being added in an amount such that the resulting granules are coated, and, if required, providing a further odour by adding scents and, if required,ensuring free-flowing properties of the agglomerates by dusting with a finely divided dusting agent.

10. A process as claimed in claim 9, wherein the carrier is initially taken in a mixer, impregnated with the organic acid and then agglomerated and coated with the covering material.

11. Use of granules as claimed in claim 1 for acid treatment and preservation of foods and animal feeds, and in silages.

12. Granules substantially as herein described with reference to the examples.

13. A process substantially as herein described with reference to the examples.